Stereochemical Aspects in the Insertion by Alkylidenemethylene Carbenoids into the α-C–H Bond of Alkoxides[1]

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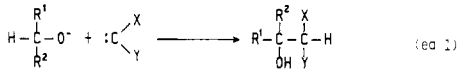
Primary alkoxides (R^1CH_2OM; M = K or Li) when treated with haloalkenes ($R^3R^4C{=}CXY$; X = Cl or Br, Y = H or Cl) in the presence of *n*-BuLi in THF at 0 °C gave allylic alcohols ($R^1CH(OH)CH{=}CR^3R^4$) through the insertion reaction of the corresponding alkylidenemethylene carbenoid ($R^3R^4C{=}C{:}\cdots LiX$) into the α-C–H bond of alkoxides. Secondary alkoxides (R^1R^2CHOM), under similar reaction conditions, gave butyl adducts ($R^1R^2C(OH)C_4H_9$) in addition to the insertion products. In particular, the C–H insertion of menthyl oxide proceeded without stereospecificity to give a mixture of the axial and equatorial insertion products. These results provided evidence for the hydride abstraction–recombination mechanism in the carbenoid insertion reaction. The regioselective, nonstereospecific insertion reaction was also observed when alkoxides were treated with separately prepared ((2,3-benzo-2-cyclohexylidene)chloromethyl)lithium at temperatures from −95 to −40 °C. The absence of H–D scrambling in crossover experiments under these reaction conditions clearly showed that the hydride abstraction–recombination mechanism proceeded within a solvent cage. An inversion of configuration on the carbenoid carbon in the hydride abstraction step was proposed on the basis of the *E*/*Z* stereoselectivity in the insertion products.

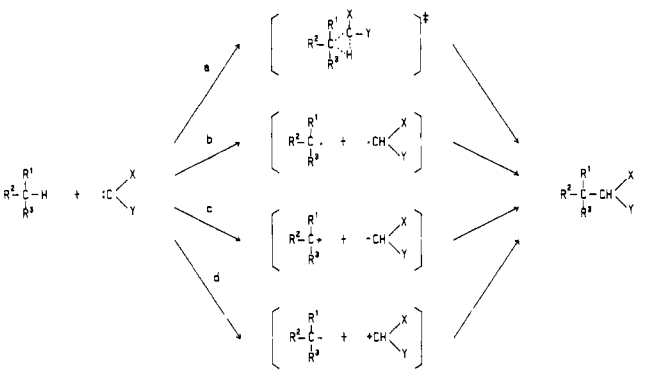
While intensive study of the stereochemistry of the addition of carbenes to carbon–carbon unsaturation has provided valuable information on its mechanism, only a limited number of reports have appeared in the study of stereochemical aspects on the C–H insertion by carbenes.[2] This has been partly due to the low regioselectivity of the C–H insertion that makes the reaction difficult to be analyzed. Recently we have reported a novel oxyanionic substituent effect[3] which promotes the carbenic insertion into the α-C–H bond of alkoxides (eq 1).[4,5] The regioselective insertion, while synthetically useful, also affords us an opportunity for mechanistic study based on the stereochemical aspects of the C–H insertion.



(eq 1)

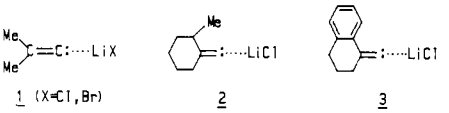
In Scheme I are shown four possible mechanisms for the C–H insertion. A concerted single-step mechanism (a) and a stepwise mechanism initiated by a hydrogen atom abstraction (b) have been extensively studied and generally ascribed to the insertion by singlet and triplet carbenes, respectively.[2] In addition, the stepwise insertion by singlet carbenes or carbenoids may possibly be initiated by a hydride abstraction (c) or a proton abstraction (d) through the participation of LUMO or HOMO of the carbenic species, respectively. Actually, a proton abstraction–recombination mechanism was demonstrated by Kirmse and co-workers in an O–H insertion by nucleophilic cycloheptatrienylidene, but not in a C–H insertion.[6] A hydride

Scheme I



abstraction–recombination mechanism was proposed by Landgrebe et al. in the dichlorocarbene insertion into the β-C–H bond of dialkylmercury compounds.[7,8] A similar stepwise insertion mechanism was recently demonstrated by us for intermolecular reaction of alkoxides with alkylidenemethylene carbenoids[1] and, following it, Ritter and Cohen reported the intramolecular system.[5c]

Herein we report the detail and further evidence for the hydride abstraction–recombination mechanism in the insertion by alkylidenemethylene carbenoids **1**–**3**[9,10] into the



1 (X=Cl, Br) **2** **3**

(1) For a preliminary account of this work, see: Harada, T.; Nozaki, Y.; Yamaura, Y.; Oku, A. *J. Am. Chem. Soc.* **1985**, *107*, 2189.

(2) (a) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971; Chapter 7. (b) Gasper, P. P.; Hammond, G. S.; *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. II, Chapter 6.

(3) (a) Evans, D. A.; Baillargeon, D. C. *Tetrahedron Lett.* **1978**, 3315, 3319, and references cited therein. (b) Steigerwald, M. L.; Goddard, W. A., III; Evans, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1994.

(4) (a) Harada, T.; Oku, A. *J. Am. Chem. Soc.* **1981**, *103*, 5965. (b) Harada, T.; Akiba, E.; Oku, A. *Ibid.* **1983**, *105*, 2771. (c) Harada, T.; Nozaki, Y.; Oku, A. *Tetrahedron Lett.* **1983**, *24*, 5665. (d) Harada, T.; Akiba, E.; Tsujimoto, K.; Oku, A. *Ibid.* **1985**, *26*, 4483. (e) Oku, A.; Yamaura, Y.; Harada, T. *J. Org. Chem.* **1986**, *51*, 3730.

(5) (a) Nilsen, N. O.; Skattebøl, L.; Sydnes, L. K. *Acta Chem. Scand., Ser. B* **1982**, *36*, 587. (b) Cohen, T.; Ritter, R. H.; Ouellette, D. *J. Am. Chem. Soc.* **1982**, *104*, 7142. (c) Ritter, R. H.; Cohen, T. *Ibid*, **1986**, *108*, 3718.

(6) Kirmse, W.; Loosen, K.; Sluma, H.-D. *J. Am. Chem. Soc.* **1981**, *103*, 5935.

(7) (a) Landgrebe, J. A.; Thurman, D. E. *J. Am. Chem. Soc.* **1969**, *91*, 1759.

(8) The similar mechanism was postulated for the Si–H insertion by alkylidenecarbene: (a) Newman, M. S.; Partrick, T. B. *J. Am. Chem. Soc.* **1970**, *91*, 4312. Recently, Gilbert et al. raised questions about the mechanism. (b) Gilbert, J. C.; Giamalva, D. H. *J. Org. Chem.* **1985**, *50*, 2586.

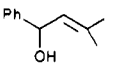
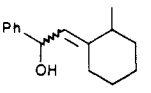
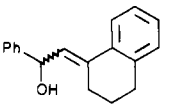
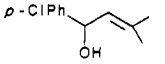
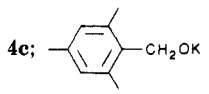
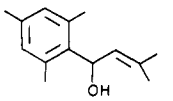
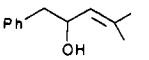
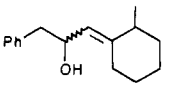
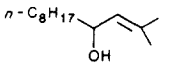
(9) For reviews, see: (a) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348. (b) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. (c) Hartzler, H. D. *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1975; Vol. II, Chapter 2.

(10) In the present paper, the name alkylidenemethylene carbenoid and (alkylidenehalomethyl)lithium are employed to express the carbene complexed with alkali metal halides and the α-haloorganolithium compounds, respectively.[11]

(11) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467.

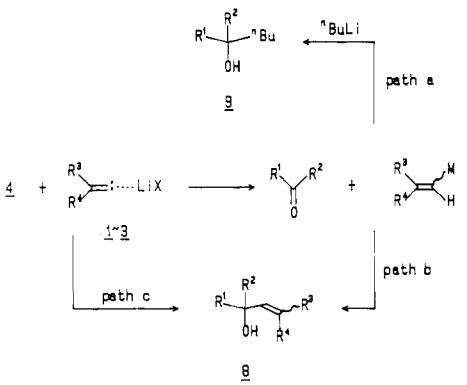
0022-3263/88/1953-3089$01.50/0

Table I. Reaction of Primary Alkoxides with Alkylidenemethylene Carbenoids at 0 °C

entry	alkoxide 4	precursor of carbenoid	product [E:Z]	yield,[a] % (convn, %)
1	**4a**; $PhCH_2OK$	**5a**	 **8a**	61 (62)
2	**4a**; $PhCH_2OK$	**5b**	**8a**	65 (73)
3	**4a**; $PhCH_2OK$	**6a**	 **8b** [1:1.1][b]	82 (49)
4	**4a**; $PhCH_2OK$	**6b**	**8b** [1:1.3][b]	95 (61)
5	**4a**; $PhCH_2OLi$	**6b**	**8b** [1:1.2][b]	65 (63)
6	**4a**; $PhCH_2OK$	**7a**	 **8c** [2.8:1]	76 (68)
7	**4b**; $p\text{-}ClC_6H_4CH_2OK$	**5a**	 **8d**	55 (60)
8[c]	**4c**; 	**5a**	 **8e**	64 (34)
9	**4d**; $PhCH_2CH_2OK$	**5a**	 **8f**	67 (42)
10	**4d**; $PhCH_2CH_2OK$	**6a**	 **8g** [1:1.5][b]	60 (47)
11	**4d**; $PhCH_2CH_2OK$	**6b**	**8g** [1:1.2][b]	54 (74)
12	**4e**; $n\text{-}C_8H_{17}CH_2OK$	**5a**	 **8h**	50 (50)

[a] Yield refers to the isolated yield based on the starting alcohol consumed. [b] These ratios were determined after oxidation of the mixture of insertion products to enone **10b,g** (see eq 3). [c] 1-(2,4,6-Trimethyl)-1-pentanol (**9a**) was obtained in 17% yield.

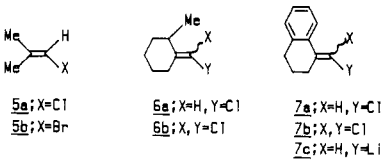
Scheme II



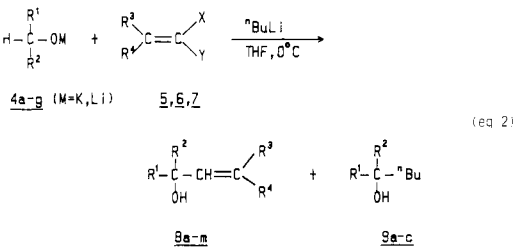
α-C–H bond of alkoxides. This evidence was provided by the stereochemical studies not only of the substrate to determine whether the insertion proceeds with retention of configuration on the carbinyl carbon of alkoxides but also of the carbenoid moiety to see whether the initial *E* or *Z* configuration of the carbenoid is retained.

Results and Discussion

Reactions of Alkoxides with Alkylidenemethylene Carbenoids at 0 °C. A mixture of potassium or lithium alkoxides **4a–g** (M = K or Li) and appropriate haloalkene (**5a,b**, **6a,b**, or **7b**) in tetrahydrofuran (THF) was treated

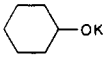
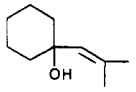
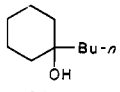
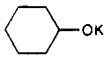
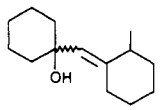
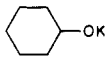
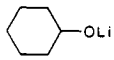
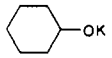
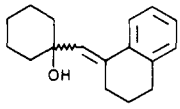
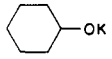
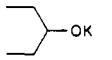
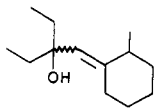
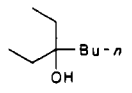
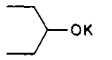


with *n*-BuLi (hexane solution) at 0 °C to give the corresponding α-C–H insertion product **8a–m** (eq 2). The results are summarized in Tables I and II for primary and secondary alkoxides, respectively.

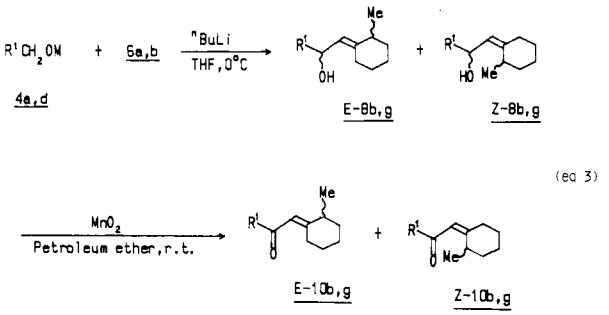


Alkylidenemethylene carbenoids **1–3** generated under these reaction conditions underwent regioselective insertion into the α-C–H bond of alkoxides as other carbenes

Table II. Reaction of Secondary Alkoxides with Alkylidenemethylene Carbenoids at 0 °C

entry	alkoxide 4	precursor of carbenoid	products (isolated yield, %) [E:Z]	
13	**4f**; 	**5a**	 **8i** (18)	 **9b** (7)
14	**4f**; 	**6a**	 **8j** [1:2.8] (18)	**9b** (7)
15	**4f**; 	**6b**	**8j** [1:2.2] (30)	**9b** (16)
16	**4f** 	**6b**	**8j** [1:2.0] (20)	**9b** (16)
17	**4f**; 	**7a**	 **8k** [2.2:1] (38)	**9b** (8)
18	**4f**; 	**7b**	**8k** [2.2:1] (29)	**9b** (5)
19	**4g**; 	**6a**	 **8m** [1.0:1] (26)	 **9c** (23)
20	**4g**; 	**6b**	**8m** [1:1.1] (33)	**9c** (12)

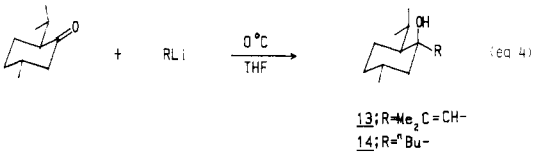
did.[4] In no case was there observed for formation of products derived from an insertion reaction into other C–H bonds of the alkoxides or into the C(2)–H bond of the solvent THF. Here, 1-chloro-, 1-bromo-, and 1,1-dichloroalkenes can be employed as precursor of the carbenoid. The insertion by the unsymmetrically substituted carbenoids **2** and **3** gave a mixture of *E* and *Z* geometrical isomers. In the reaction of primary alkoxides with carbenoid **2** (Table I, entries 3, 4, 5, 10, and 11), each isomer (*E* or *Z*) of the insertion products consisted of a pair of diastereomers rendering the product analysis difficult. Therefore, the mixture of insertion products was oxidized with MnO_2[12] to the *E*/*Z* mixture of enone **10b,g** and analyzed (eq 3).



(eq 3)

In the reactions of secondary alkoxides (Table II), the yields of insertion products **8** decreased significantly in comparison with those of primary alkoxides; instead, a substantial amount of the butyl adduct **9** was formed. The formation of **9** suggests an intermediacy of a ketone, which is trapped by *n*-BuLi under the reaction conditions (Scheme II, path a); it also suggests that an intermolecular hydride transfer from the carbon of secondary alkoxides to the carbenic carbon of alkylidenemethylene carbenoids takes place to give an intermediate ketone and a vinylic anion. Therefore, it is reasonable to assume that the insertion product **8** is formed by the hydride abstraction–recombination mechanism (Scheme II, path b).

Reactions of Menthyl Oxide (11) with Isopropylidenemethylene Carbenoid (1) at 0 °C. In order to confirm the proposed hydride abstraction–recombination mechanism by examining the stereochemistry of the insertion reaction, we chose menthyl oxide (**11**) and neomenthyl oxide (**15**) as suitable substrates. The choice was founded on their sterically fixed α-C–H bond which tells us a configurational change after the reaction and also on the finding that menthone, the intermediate of the stepwise insertion, undergoes an exclusive equatorial attack by (2-methylpropenyl)lithium or *n*-BuLi (eq 4).[13]



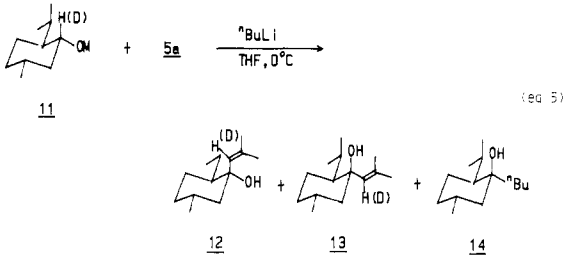
(eq 4)

Previously we demonstrated that the insertion reactions by (phenylthio)carbene (or carbenoid)[4a] and vinylidene carbene (or carbenoid)[4c] proceeded with retention of configuration. In contrast to these, isopropylidenemethylene carbenoid (**1**) reacted at 0 °C with potassium menthyl oxide (**11**; M = K) nonstereospecifically to give a mixture of stereoretaining axial insertion product **12**, stereoinverted equatorial insertion product **13**, and equatorial butyl ad-

(12) Attenburrow, A.; Cameron, A. F. B.; Chapman, J. H.; Evans, R. M.; Hems, B. A.; Jansen, A. B. A., Walker, T. *J. Chem. Soc.* **1952**, 1094.

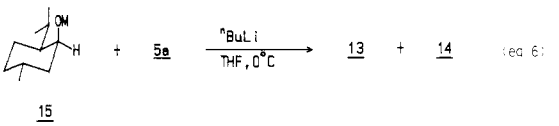
(13) Ashby, E. C.; Laemmele, J. T. *Chem. Rev.* **1975**, *75*, 521 and references cited therein.

duct **14** in the ratio of 24:4:72 (total yield 56%, based on 37% conversion of menthol) (eq 5). When a THF solution



(eq 5)

of lithium menthyl oxide (**11**; M = Li) (2.0 equiv) and **5a** was treated with *n*-BuLi at −85 °C and then warmed to room temperature, the relative yield of **13** increased in comparison with those of **12** and **14** (**12**:**13**:**14** = 47:12:41, total yield 30%). Contrastingly, the reaction of potassium neomenthyl oxide (**15**; M = K), the epimer of **11**, at 0 °C (eq 6) gave **13** and **14** (51:49) in 46% yield, being consistent with the hydride abstraction mechanism in which the recombination and the addition of *n*-BuLi take place exclusively on the equatorial face of the intermediate menthone to give **13** and **14**, respectively.

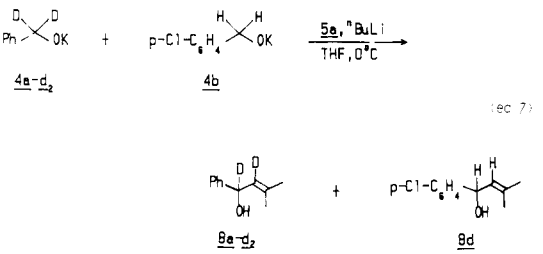


(eq 6)

While the above observations support the participation of the hydride abstraction–recombination mechanism, there are other possible routes that deserve consideration. First, the alkoxide of the insertion product **12** may undergo a fragmentation reaction under the reaction conditions to generate menthone and 2-methylpropenyl anion. However, the following control experiment showed this hypothesis to be untenable. When the potassium alkoxide of **12** was treated with *n*-BuLi in THF at 0 °C for 30 min, the formation of neither stereoisomer **13** nor butyl adduct **14** was detected by capillary GLC analysis. Second, (2-methylpropenyl)lithium may be generated mainly from **5a** and *n*-BuLi. This was also ruled out by a deuterium-labeling experiment where the reation of lithium menthyl-*1-d* oxide (**11**-*d*, *d* content > 95%) gave **12**-*d* and **13**-*d* with >95% and 84% deuterium incorporation, respectively, at the vinylic position (eq 5).[14]

Thus, it is clear that stereoinverted equatorial insertion product **13** obtained from menthyl oxide (**11**) was produced by the hydride abstraction–recombination mechanism (Scheme II, path b). On the other hand, the stereoretaining axial insertion product **12** can be formed either through a concerted (path c) or through a hydride abstraction followed by a rapid recombination within a solvent cage (path b).

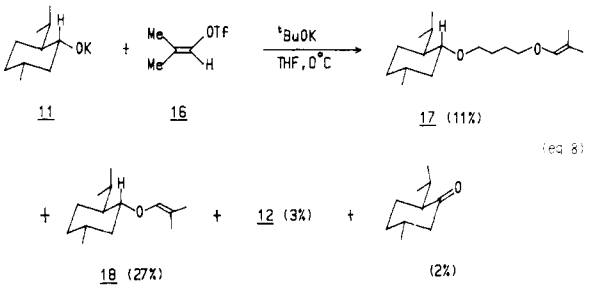
In contrast to secondary alkoxides, primary alkoxides behaved in a different way. For example, their reactions at 0 °C gave no butyl adduct except entry 8 in Table I. Moreover, even at 0 °C, no H–D scrambling was observed in the reaction of a mixture of **4a**-*d* (M = K) and **4b** (M = K) with carbenoid **1** (eq 7). Therefore, primary alkoxides undergo insertion through either a concerted mechanism (Scheme II, path c) or a hydride abstraction which is followed by a rapid recombination within a solvent cage (path b). The reaction of **1** with sterically hindered 2,4,6-trimethylbenzyl oxide (**4c**; M = K) was exceptional



(eq 7)

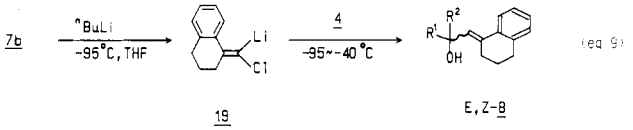
but informative: it gave butyl adduct **9a** (17% yield) together with insertion product **8e** (entry 8). If path b is the case, this anomaly can be understood in terms of the steric effects of the trimethylphenyl group which retards the recombination. If path c is the case, it can be suppressed by bulky substituents and, instead, the hyride abstraction becomes dominant.

The reaction conditions employed here for the generation of carbenic species suggest that the reactions proceed not through a free carbene but through a carbenoid.[9] This can be verified by comparison of the above reactions with those of a free (or unencumbered) carbene[9b] generated from 2-methylpropenyl triflate (**16**):[15] the reaction of alkoxide **11** (M = K) with **16** and *t*-BuOK in THF gave 4-(methyloxy)butyl 2-methylpropenyl ether (**17**) as a major product (11%) (eq 8),[16] whereas **17** was absent in the reaction with **5a**,**b** and *n*-BuLi.



(eq 8)

Reaction of Alkoxides with (2,3-Benzo-2-cyclohexylidene)methylene Carbenoid (3) at Low Temperatures. As indicated in the reaction of lithium menthyl oxide (**11**; M = Li) with **5a** and *n*-BuLi at −85 °C, (1-chloro-2-methylpropenyl)lithium is unstable at this temperature and undergoes carbenoid insertion reactions in competition with the addition of *n*-BuLi to the intermediately formed menthone. On the other hand, ((2,3-benzo-2-cyclohexylidene)chloromethyl)lithium (**19**) is stable at −95 °C (vide infra)[17] and, therefore, can be prepared from **7** and *n*-BuLi as a *n*-BuLi-free solution, thus avoiding the butyl adduct formation. Indeed, when the dark blue solution of **19** prepared by the reaction of **7b** with *n*-BuLi in THF at −95 °C was mixed with a THF solution of a lithium alkoxide (2 equiv), the C–H insertion reaction did not proceed appreciably at −95 °C (entry 3 in Table III). When the resulting mixture was warmed from −95 °C to −40 °C over the period of 1.5 h, a mixture of the insertion products (*E* and *Z* isomer) was obtained but no butyl adduct **9** (eq 9 and Table III).



(eq 9)

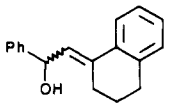
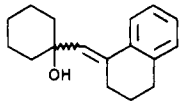
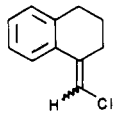
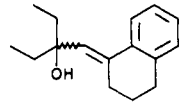
(14) A slight decrease in the deuterium content in **13**-*d* might suggest the generation of (2-methylpropenyl)lithium by the reaction of **5a** with *n*-BuLi.

(15) Stang, P. J.; Mangum, M. G.; Fox, D. P.; Haak, P. *J. Am. Chem. Soc.* **1974**, *96*, 4562.

(16) (a) Gilbert, J. C.; Weerasooriya, Y. *Tetrahedron Lett.* **1980**, *21*, 2041; (b) *J. Org. Chem.* **1982**, *47*, 1837.

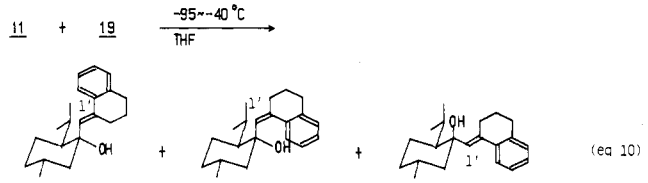
(17) Köbrich, G.; Ansari, F. *Chem. Ber.* **1967**, *100*, 2011.

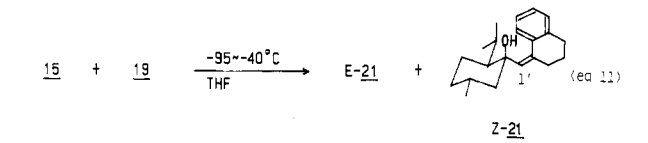
Table III. Reaction of Lithium Alkoxides with ((2,3-Benzo-2-cyclohexylidene)chloromethyl)lithium (19) at Low Temperatures

entry	alkoxides 4 (M = Li)	product	yield, %	[E:Z]
1	4a	 **8c**	49	[3.6:1]
2	4f	 **8k**	40	[2.7:1]
3[a]	4f	 **7a**	78	[8.2:1]
4	4g	 **8n**	45	[4.7:1]

[a] The reaction was performed at −95 °C for 6 h. Small amount (<5%) of insertion product **8k** was obtained.

Under similar reaction conditions, the stereochemical course of the C–H insertion of menthyl oxide (**11**) and neomenthyl oxide (**15**) was examined (eq 10 and 11). In

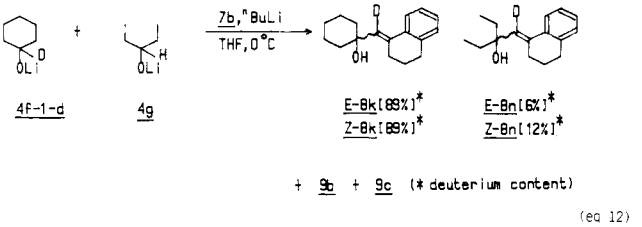




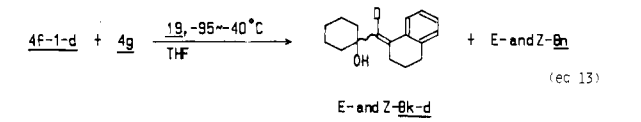
the reaction of **11** (M = Li) with **19**, a mixture of (*E*)-**20**, (*Z*)-**20**, and (*E*)-**21** was obtained in the ratio of 39:14:47 (total yield 26%). The formation of equatorial insertion product (*E*)-**21** again provided evidence of the hydride abstraction–recombination mechanism under these reaction conditions. On the other hand, in the reaction of **15** (M = Li) only the equatorial insertion products ((*E*)- and (*Z*)-**21**) (53%) were obtained with a high *E* selectivity ((*E*)-**21**:(*Z*)-**21** = 97:3).

Since hydride abstraction by the carbenoids from the α carbon of an alkoxide intermediately produces a ketone and a vinylic anion, a question arises whether the subsequent recombination step proceeds within or out of a solvent cage. The formation of butyl adducts in the reaction of 0 °C (see e.g. Table II, **9b** and eq 5) implies that the solvent cage may not be strong enough to exclude the out-of-cage recombination of the intermediates under these conditions. To clarify this further, we performed the following crossover experiments.

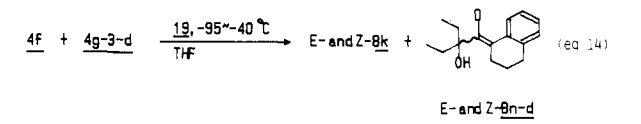
When a mixture of cyclohexyl-*1-d* oxide (**4f**-*d*; M = Li), 3-pentyl oxide (**4g**; M = Li), and **7b** was treated with *n*-BuLi in THF at 0 °C, deuterium scrambling was observed to some extent in the C–H insertion products **8** besides the formation of **9b** and **9c** (eq 12). Therefore, considerable leakage of the reaction intermediates from a solvent cage occurred at 0 °C.



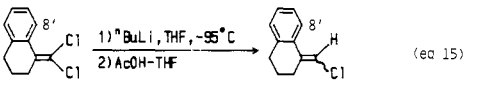
It is well anticipated that the in-cage recombination pathway becomes favorable at low temperatures due to the increase of solvent viscosity. In sharp contrast to the scrambling at 0 °C, the same crossover reaction with **19** at −95 to −40 °C gave insertion product **8k**-*d* in which the proton incorporation at the vinylic position was very low (<3%) (eq 13).[18] Similarly the reaction of a mixture of

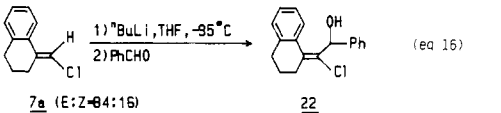


4f (M = Li) and **4g**-*d* (M = Li) with **19** gave **8n**-*d* in which the proton incorporation was less than 2%[18] (eq 14). On the reasonable assumption that the reactivities of secondary alkoxides toward hydride abstraction are similar, the above results, together with the lack of stereospecificity in the reaction of menthyl oxide (**11**), clearly mean that the stepwise insertion proceeds almost exclusively within a solvent cage at low temperatures.



***E*/*Z* Selectivity in the C–H Insertion Products 20 and 21.** ((2,3-Benzo-2-cyclohexylidene)chloromethyl)-lithium (**19**) is stable at −95 °C as shown by the following experiments. The treatment of dichloride **7b** with *n*-BuLi at −95 °C for 1 h followed by protonation with cold AcOH–THF at the same temperature gave monochloride **7a** (*E*:*Z* = 61:1) in 89% yield (eq 15). Moreover, the reaction





of benzaldehyde with **19** which was prepared from **7a** (*E*:*Z* = 84:16) and *n*-BuLi (at −95 °C for 6.5 h) gave only the *E* isomer of adduct **22** (88%) with recovery of **7a** (6%; *E*:*Z* = 6:1) (eq 16). Thus, (*E*)-**19** is selectively formed and stable under these conditions. Köbrich et al. reported the presence of an equilibrium between (*E*)- and (*Z*)-(2-aryl-1-chloro-1-propenyl)lithium under similar conditions.[17] Since kinetically controlled formation of (*E*)-**19** by the

(18) These values were determined by 200-MHz ^{1}H NMR measurement. Determination of the deuterium content by mass spectral analysis was difficult due to the low intensity of the molecular ion peaks.

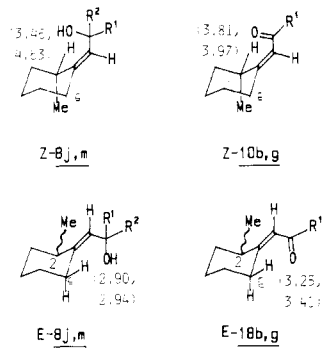
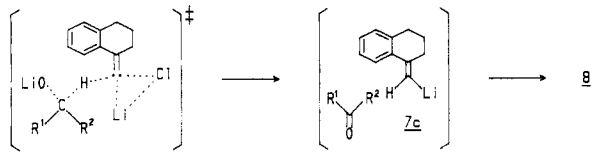


Figure 1.

Scheme III



attack of *n*-BuLi at the more hindered endo chlorine atom of **7b** is unlikely, we can reasonably conclude that a thermodynamic equilibrium which strongly favors the *E* isomer is established between (*E*)- and (*Z*)-**19** under these conditions.

One purpose in the present study is to clarify the transition-state geometry in the C–H insertion reaction. In this regard, the *E*/*Z* stereoselectivity observed in the reaction of unsymmetrically substituted alkylidenemethylene carbenoids will provide us with valuable information.[4e,8] Despite of the less informative result with **2**, the reaction of (2,3-benzo-2-cyclohexylidene)methylene carbenoid (**3**) generated from **19** at low temperatures provided valuable stereochemical information about the hydride abstraction step. In the reaction of menthyl oxide (**11**) with **19**, three insertion products, (*E*)-**20**, (*Z*)-**20**, and (*E*)-**21**, were obtained in the ratio of 39:14:47 (eq 10). Although the mechanism of formation of (*Z*)-**20** is not yet rigorously elucidated, we can deduce from this result that in the hydride abstraction step the *E* isomer of ((2,3-benzocyclohexylidene)methyl)lithium (**7c**) is generated with 74–100% selectivity from the thermodynamically stable (*E*)-**19** (see the preceding paragraph). A highly selective formation of (*E*)-**21** in the reaction of neomenthyl oxide (**15**) is also suggestive of the selective formation of the *E* isomer of **7c** in the hydride abstraction step. In view of the recent study by Walborsky et al.,[19] who elegantly demonstrated that alkyllithium displaces the chloride or bromide ion on the alkylidenemethylene carbenoid with inversion of configuration, we can reasonably conclude that the hydride abstraction proceeds with inversion of configuration on the carbenoid carbon as depicted in Scheme III.

Determination of the Stereochemistry. *E* and *Z* structures of insertion products **8j** and **8m** and their oxidized derivatives **10b** and **10g** obtained from carbenoid **2** were determined by ^{1}H NMR analysis (Figure 1). Appearance of the methine proton attached to C(2) of **10b** and **10g** or **8j** and **8m** as a multiplet at δ 3.4–4.0 was used as a probe of the *Z* isomers where the proton is cis to the carbonyl or the hydroxyl group, respectively.[20] On the other hand, appearance of the equatorial methylene proton at C(6) as a multiplet at δ 2.9–3.4 was used as a probe for *E* isomers.

Table IV. ^{1}H NMR Chemical Shifts of Vinylic Protons in Insertion Protducts by (2,3-Benzo-2-cyclohexylidene)methylene Carbenoid (3)

E isomer	chem shift (ppm)	*Z* isomer	chem shift (ppm)	$\Delta\delta$
(*E*)-**8c**	6.21	(*Z*)-**8c**	5.70	0.51
(*E*)-**8k**	6.04	(*Z*)-**8k**	5.51	0.53
(*E*)-**8n**	5.91	(*Z*)-**8n**	5.34	0.57
(*E*)-**20**	6.20	(*Z*)-**20**	5.77	0.43
(*E*)-**21**	5.90	(*Z*)-**21**	5.36	0.54

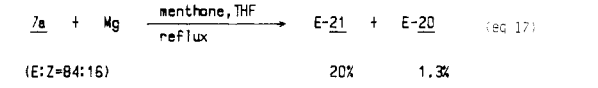
Table V. ^{13}C NMR Chemical Shifts of C(1′) in Insertion Products of 11 and 15

axial insertn prod	chem shift (ppm)	equatorial insertn prod	chem shift (ppm)	$\Delta\delta$
12	126.2	**13**	132.2 (or 132.8)	6.0 (or 6.6)
(*E*)-**20**	125.9[a]	(*E*)-**21**	132.1[a]	6.2
(*Z*)-**20**	128.0[a]	(*Z*)-**21**	134.0[a]	6.0

[a] The assignment was performed by utilizing a selective proton decoupling technique.

As shown in Table IV, the olefinic proton of the *E* isomer of insertion products by carbenoid **3** appeared at a lower field (ca. 0.5 ppm) than that of the *Z* isomer due to the deshielding effect of the benzene ring. The stereochemistry of four isomeric products ((*E*)- and (*Z*)-**20** and (*E*)- and (*Z*)-**21**) obtained in the reactions of both **11** and **15** was also determined on the basis of the same criteria.

The equatorial/axial stereochemistry of **12**, **13**, (*E*)-**20**, (*Z*)-**20**, (*E*)-**21**, and (*Z*)-**21** was determined by the ^{13}C NMR spectra where the axial vinylic carbon atom C(1′) (see eq 9 and 10) appeared at a field higher than the equatorial one.[21] Chemical shifts of C(1′) in these compounds are summarized in Table V. The present assignments were verified further by the highly selective formation of **13** and (*E*)-**21** in the reaction of menthone with (2-methylpropenyl)lithium (eq 4) and ((2,3-benzo-2-cyclohexylidene)methyl)magnesium chloride (eq 17), respectively.



In the ^{1}H NMR spectra of dichloride **7b** and monochloride (*Z*)-**7a**, protons attached to C(8′) (see eq 15 and 16) appeared at considerably low field (δ 7.86 and 8.20, respectively) due to the nearby chlorine atom. In the ^{1}H NMR spectrum of **22** which was obtained by the reaction of (chloromethyl)lithium **19** with benzaldehyde (eq 16), such a deshielding effect of chlorine atom was not observed, and the signal of C(8′) proton appeared at δ 7.32. Therefore the geometry of **22** was assigned as *E*.

Experimental Section

Infrared spectra were measured on a JASCO IRA-1 grating spectrophotometer. Unless otherwise noted, ^{1}H NMR and ^{13}C NMR spectra were obtained with a Varian XL-200 spectrophotometer in $CDCl_3$ (Me_4Si standard). Mass spectra were measured at 70 eV on a Hitachi M-80 mass spectrometer. GLC analyses were performed with a Shimazu GC 9A chromatograph utilizing a flame ionization detector on a OV-101 (30 m) or PEG-20M (30 m) capillary column. Unless otherwise noted, flash chromatography was performed by using silica gel (Wakogel C-300) as an

(19) (a) Duraisamy, M.; Walborsky, H, M. *J. Am. Chem. Soc.* **1984**, *106*, 5035. (b) Rachon, J.; Goedken, V.; Walborsky, H. M. *Ibid.* **1986**, *108*, 7435. (c) Walborsky, H. M.; Duraisamy, M. *Tetrahedron Lett.* **1985**, *26*, 2743.

(20) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1983**, *105*, 3252 and references cited therein.

(21) Gaudemer, A. *Stereochemistry*; Kangan, H. B., Ed.; Georg Thieme Publishers: Stuttgart, 1977; Vol. I, p 106.

absorbent and ethyl acetate in petroleum ether as an eluent, whose concentration is indicated in the parentheses. Medium-pressure column chromatography was performed by using a Merck Lobar column packed with 40–63-μm Li-Chroprep SI 60. The reactions at −85 °C were performed by using a Neslab Cryocool CC-80 immersion cooler. THF was dried and distilled from sodium benzophenone ketyl prior to use.

1-Bromo-2-methylpropene (**5b**)[22] and (*E* and *Z*)-chloro(2-methylcyclohexylidene)methane (**6a**; *E*:*Z* = 96:4)[23] were prepared by the literature procedures. 2,4,6-Trimethylbenzyl alcohol was prepared by $LiAlH_4$ reduction of 2,4,6-trimethylbenzaldehyde.[24]

(*E* and *Z*)-(2,3-Benzo-2-cyclohexylidene)chloromethane (**7a**; *E*:*Z* = 84:16) was prepared by following the general procedure of Miyano et al.[23] **7a**; bp 95 °C/1 mmHg; ^1H NMR of *E* isomer δ 1.85 (2 H, quint, *J* = 6.2 Hz), 2.68 (2 H, dt, *J* = 2.2 and 6.2 Hz), 2.77 (2 H, t, *J* = 6.2 Hz), 6.61 (1 H, t, *J* = 2.2 Hz), 7.08–7.28 (3 H, m), 7.45 (1 H, m); ^1H NMR of *Z* isomer δ 1.9 (2 H, m), 2.47 (2 H, m), 2.88 (2 H, t, *J* = 6.6 Hz), 6.11 (1 H, t, *J* = 1.0 Hz), 7.08–7.28 (3 H, m), 8.20 (1 H, m); IR (liquid film) 1615 (s), 920 (s), 815 (s), 780 (s), 750 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 180 (M^+, $C_{11}H_{11}{}^{37}Cl$, 33), 178 (M^+, $C_{11}H_{11}{}^{35}Cl$, 100), 143 (60), 128 (65), 115 (49); exact mass calcd for $C_{11}H_{11}{}^{37}Cl$ 180.0520 and $C_{11}H_{11}{}^{35}Cl$ 178.0550 (found 180.0516 and 178.0552).

Dichloro(2-methylcyclohexylidene)methane (**6b**) and (2,3-benzo-2-cyclohexylidene)dichloromethane (**7b**) were prepared according to the general procedure of Speziale et al.[25] **6b**: bp 85 °C/20 mmHg; ^1H NMR (60 MHz, CCl_4) δ 1.10 (3 H, d, *J* = 7.2 Hz), 1.33–2.33 (6 H, m), 2.56–3.46 (3 H, m); IR (liquid film) 905 (s), 845 cm^{-1} (s). **7b**: ^1H NMR δ 1.79 (2 H, quint, *J* = 6.0 Hz), 2.65 (2 H, t, *J* = 6.0 Hz), 2.69 (2 H, t, *J* = 6.0 Hz), 7.10–7.29 (3 H, m), 7.86 (1 H, m); IR (liquid film) 935 (s), 865 (s), 760 (s), 745 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 216 (M^+, $C_{11}H_{10}{}^{37}Cl_2$, 10), 214 (M^+, $C_{11}H_{10}{}^{37}Cl^{35}Cl$, 58), 212 ($M^+$, $C_{11}H_{10}{}^{35}Cl_2$, 89), 177 (66), 162 (20), 149 (16), 141 (100), 129 (64), 115 (53); exact mass calcd for $C_{11}H_{10}{}^{37}Cl_2$ 216.0101, $C_{11}H_{10}{}^{37}Cl^{35}Cl$ 214.0131, and $C_{11}H_{10}{}^{35}Cl_2$ 212.0161 (found 216.0099, 214.0129, and 212.0152).

General Procedure for the Reaction of Alkoxides with Alkylidenemethylene Carbenoids. A THF suspension of potassium alkoxide **4** (M = K) and a THF solution of lithium alkoxide **4** (M = Li) were prepared by the reaction of the corresponding alcohol with KH (oil free, 1.0 equiv) and *n*-BuLi (1.0 equiv), respectively, at 0 °C for 0.5 h under a nitrogen atmosphere. To the mixture of alkoxide **4** (2 mmol) in THF (5 mL) was added successively an appropriate precursor of a carbenoid (**5a,b**, **6a,b**, or **7b**) (3.2–4.0 mmol) and *n*-BuLi (3.2–4.0 mmol) at 0 °C. After being stirred for 5 min, the reaction mixture was quenched by the addition of water and extracted twice with ethyl acetate. Concentration of the dried (sodium sulfate) extracts in vacuo followed by purification by flash chromatography gave the insertion product **8** and/or butyl adduct **9**. If necessary, separation of *E* and *Z* isomers of **8** was performed by using medium-pressure column chromatography. In the reactions of primary alkoxides with 2-methylcyclohexylidene carbenoid **2** (Table I, entries 3, 4, 5, 10, and 11), a mixture of stereoisomers obtained after flash chromatography was treated with MnO_2 in petroleum ether for 15 h at the room temperature.[12] The filtrate of the reaction mixture was purified by flash chromatography to give enone **10b,g** in 72% (entry 3), 60% (entry 4), 85% (entry 5), 41% (entry 10), and 56% (entry 11). The spectral data of new compounds are as follows.

3-Methyl-1-phenyl-2-butenol (8a): ^1H NMR δ 1.74 (3 H, br s), 1.79 (3 H, br s), 1.90 (1 H, br), 5.43 (2 H, m), 7.37 (5 H, m); IR (liquid film) 3260 (br), 1680 (m), 1460 (s), 1040 (s), 865 (m), 760 (m), 750 (m), 700 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 162 (M^+, <1), 144 (46), 129 (100), 128 (55); exact mass calcd for $C_{11}H_{14}O$ 162.1045 (found 162.1038).

(*E*)-2-(2-Methylcyclohexylidene)-1-phenylethanone ((*E*)-10b): ^1H NMR δ 1.16 (3 H, d, *J* = 7.2 Hz), 1.20–1.90 (6 H, m), 2.17 (1 H, m), 2.34 (1 H, m), 3.25 (1 H, br d, *J* = 12.4 Hz), 6.52 (1 H, s), 7.36–7.60 (3 H, m), 7.96 (2 H, m); IR (liquid film) (a mixture of *E* and *Z* isomers) 1665 (s), 1615 (s), 865 (s), 835 (s), 785 (s), 710 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 214 (M^+, 36), 199 (8), 185 (3), 171 (8), 157 (35), 105 (100), 77 (48); exact mass calcd for $C_{15}H_{18}O$ 214.1358 (found 214.1355).

(*Z*)-2-(2-Methylcyclohexylidene)-1-phenylethanone ((*Z*)-10b): ^1H NMR δ 1.21 (3 H, d, *J* = 6.8 Hz), 1.33–1.82 (5 H, m), 1.93 (1 H, m), 2.17 (1 H, br d, *J* = 13.4 Hz), 2.51 (1 H, ddt, *J* = 1.6, 5.0, and 13.4 Hz), 3.81 (1 H, m), 6.55 (1 H, d, *J* = 1.6 Hz), 7.83–7.57 (3 H, m), 7.88–8.00 (2 H, m); mass spectrum, *m*/*z* (relative intensity) 214 (M^+, 56), 199 (16), 185 (9), 171 (14), 157 (56), 105 (100), 77 (80); exact mass calcd for $C_{15}H_{18}O$ 214.1358 (found 214.1355).

(*E*)-2-(2,3-Benzo-2-cyclohexylidene)-1-phenylethanol ((*E*)-8c): ^1H NMR δ 1.75–2.15 (3 H, m), 2.56 (1 H, m), 2.68–2.96 (3 H, m, including t (2 H, *J* = 6.4 Hz) at 2.80), 5.68 (1 H, d, *J* = 8.5 Hz), 6.21 (1 H, td, *J* = 1.7 and 8.5 Hz), 7.00–7.53 (8 H, m), 7.62 (1 H, m); IR (liquid film) 3450 (br), 1635 (s), 1605 (s), 1250 (s), 1060 (s), 965 (s), 910 (s), 755 (s), 695 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 250 (M^+, 4), 232 (33), 217 (13), 173 (12), 130 (100), 91 (32), 77 (36); exact mass calcd for $C_{18}H_{18}O$ 250.1358 (found 250.1361).

(*Z*)-2-(2,3-Benzo-2-cyclohexylidene)-1-phenylethanol ((*Z*)-8c): ^1H NMR δ 1.79–2.09 (3 H, m), 2.36–2.62 (2 H, m), 2.84 (2 H, t, *J* = 6.7 Hz), 5.61 (1 H, d, *J* = 9.4 Hz), 5.70 (1 H, td, *J* = 1.1 and 9.4 Hz), 7.00–7.55 (9 H, m); IR (liquid film) 3420 (br), 1260 (s), 915 (s), 7745 (s), 700 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 250 (M^+, 4), 232 (8), 217 (3), 178 (9), 130 (100), 91 (24), 77 (30); exact mass calcd for $C_{18}H_{18}O$ 250.1358 (found 250.1359).

3-Methyl-1-(4-chlorophenyl)-2-butenol (8d): ^1H NMR (60 MHz) δ 1.71 (6 H, br s), 2.84 (1 H, br), 5.23 (2 H, br s), 7.19 (4 H, m); IR (liquid film) 3340 (br), 1680 (m), 1040 (s), 870 (m), 840 (m), 810 cm^{-1} (m); exact mass calcd for $C_{11}H_{13}O^{35}Cl$ 196.0656 (found 196.0657).

3-Methyl-1-(2,4,6-trimethylphenyl)-2-butenol (8e): ^1H NMR δ 1.3 (1 H, br), 1.76 (3 H, d, *J* = 1.2 Hz), 1.79 (3 H, d, *J* = 1.2 Hz), 2.27 (3 H, s), 2.44 (6 H, s), 5.67 (1 H, sept d, *J* = 1.2 and 8.8 Hz), 5.83 (1 H, br d, *J* = 8.8 Hz), 6.85 (2 H, s); IR (liquid film) 3350 (br), 1615 (m), 1040 (m), 990 (m), 915 (m), 850 (s), 740 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 204 (M^+, 4), 189 (48), 171 (24), 147 (100); exact mass calcd for $C_{14}H_{20}O$ 204.1514 (found 204.1513).

4-Methyl-1-phenyl-3-penten-2-ol (8f): ^1H NMR (60 MHz) δ 1.55 (3 H, d, *J* = 1.5 Hz), 1.70 (3 H, d, *J* = 1.5 Hz), 1.74 (1 H, br), 2.77 (2 H, d, *J* = 6.5 Hz), 4.55 (1 H, td, *J* = 6.5 and 8.5 Hz), 5.22 (1 H, m), 7.23 (5 H, m); IR (liquid film) 3370 (br), 1680 (m), 1030 (s), 850 (m), 830 (m), 750 (m), 700 cm^{-1} (m); mass spectrum, *m*/*z* (relative intensity) 176 (M^+, 1), 158 (60), 143 (100), 129 (44).

(*E*)-1-(2-Methylcyclohexylidene)-3-phenylpropan-2-one ((*E*)-10g): ^1H NMR δ 0.99 (3 H, d, *J* = 6.4 Hz), 1.00–2.80 (8 H, m), 3.41 (1 H, br d, *J* = 12.4 Hz), 3.72 (2 H, s), 5.98 (1 H, s), 7.15–7.38 (5 H, m); IR (liquid film) (a mixture of *E* and *Z* isomers) 1700 (s), 1625 (s), 945 (s), 855 (s), 715 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 228 (M^+, 3), 137 (100), 91 (55); exact mass calcd for $C_{16}H_{20}O$ 228.1515 (found 228.1520).

(*Z*)-1-(2-Methylcyclohexylidene)-3-phenylpropan-2-one ((*Z*)-10g): ^1H NMR δ 1.08 (3 H, d, *J* = 7.2 Hz), 1.10–2.02 (7 H, m), 2.36 (1 H, ddt, *J* = 1.6, 5.0, and 13.6 Hz), 3.67 (2 H, s), 3.97 (1 H, m), 5.94 (1 H, d, *J* = 1.6 Hz), 7.14–7.39 (5 H, m); mass spectrum, *m*/*z* (relative intensity) 228 (M^+, 7), 137 (100), 91 (61); exact mass calcd for $C_{16}H_{20}O$ 228.1515 (found 228.1516).

2-Methyl-2-dodecen-4-ol (8h): ^1H NMR (60 MHz) δ 0.88 (3 H, br t, *J* = ~7 Hz), 1.3 (12 H, m), 1.66 (3 H, d, *J* = 1.5 Hz), 1.70 (3 H, d, *J* = 1.5 Hz), 2.23 (1 H, br), 4.18 (1 H, td, *J* = 6.0 and 8.5 Hz, 5.09 (1 H, m); IR (liquid film) 3340 (br), 1690 (m), 1390 (m), 990 (m), 850 cm^{-1} (m); mass spectrum, *m*/*z* (relative intensity) 184 (M^+, 2), 169 (18), 166 (44), 84 (100), 81 (100); exact mass calcd for $C_{13}H_{26}O$ 184.1828 (found 184.1827).

1-(2-Methyl-1-propenyl)cyclohexanol (8i): ^1H NMR (60 MHz, CCl_4) δ 1.0–2.0 (11 H, m, including d (3 H, *J* = 1.5 Hz) at 1.67 and d (3 H, *J* = 1.5 Hz) at 1.84), 5.22 (1 H, sept, *J* = 1.5 Hz); IR (liquid film) 3420 (br), 1670 (m), 1060 (m), 980 (m), 960 (m), 920 cm^{-1} (m); mass spectrum, *m*/*z* (relative intensity) 154 (M^+, 19), 139 (21), 136 (21), 120 (60), 82 (100).

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(*E*)-1-[(2-Methylcyclohexylidene)methyl]cyclohexanol ((*E*)-8j): ^{1}H NMR δ 1.00 (3 H, d, J = 6.9 Hz), 1.05–2.18 (19 H, m), 2.94 (1 H, br d, J = 12.5 Hz), 5.19 (1 H, s); IR (liquid film) (a mixture of E and Z isomers) 3470 (br), 1670 (s), 1065 (s), 985 (s), 965 (s), 845 (s), 800 (s), 775 cm^{-1} (s); mass spectrum, m/z (relative intensity) 208 (M$^+$, 4.3), 190 (6), 137 (21), 113 (100); exact mass calcd for $C_{14}H_{24}O$ 208.1828 (found 208.1826).

(*Z*)-1-[(2-Methylcyclohexylidene)methyl]cyclohexanol ((*Z*)-8j): ^{1}H NMR δ 1.08 (3 H, d, J = 7.2 Hz), 1.10–2.14 (18 H, m), 2.24 (1 H, ddt, J = 1.8, 4.4, and 13.3 Hz), 3.46 (1 H, m), 5.19 (1 H, d, J = 1.8 Hz); mass spectrum, m/z (relative intensity) 208 (M$^+$, 25), 190 (36), 147 (29), 137 (100); exact mass calcd for $C_{14}H_{24}O$ 208.1828 (found 208.1826).

(*E*)-1-[(2,3-Benzo-2-cyclohexylidene)methyl]cyclohexanol ((*E*)-8k): ^{1}H NMR δ 1.21–1.91 (13 H, m), 2.71 (2 H, t, J = 6.8 Hz), 2.88 (2 H, dt, J = 1.4 and 6.8 Hz), 6.04 (1 H, t, J = 1.4 Hz), 7.00–7.20 (3 H, m), 7.54 (1 H, m); IR (liquid film) 3400 (br), 1630 (m), 1600 (m), 1165 (s), 1055 (s), 1035 (s), 980 (s), 960 (s), 915 (s), 845 (s), 755 (s), 725 cm^{-1} (s); mass spectrum, m/z (relative intensity) 242 (M$^+$, 25), 224 (18), 199 (10), 185 (100), 171 (39), 130(92); exact mass calcd for $C_{17}H_{22}O$ 242.1672 (found 242.1672). Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.13; H, 9.32.

(*Z*)-1-[(2,3-Benzo-2-cyclohexylidene)methyl]cyclohexanol ((*Z*)-8k): ^{1}H NMR δ 1.11–1.79 (11 H, m), 1.88 (2 H, quint, J = 6.7 Hz), 2.37 (2 H, dt, J = 1.1 and 6.7 Hz), 2.76 (2 H, t, J = 6.7 Hz), 5.51 (1 H, t, J = 1.1 Hz), 7.00–7.29 (3 H, m), 7.76 (1 H, m); IR (liquid film) 3550 (sh), 3420 (br), 1600 (s), 1050 (s), 1040 (s), 955 (s), 760 (s), 730 cm^{-1} (s); mass spectrum, m/z (relative intensity) 242 (M$^+$, 19), 224 (10), 199 (10), 185 (100), 171 (36), 130 (83); exact mass calcd for $C_{17}H_{22}O$ 242.1672 (found 242.1674).

(*E*)-3-[(2-Methylcyclohexylidene)methyl]-3-pentanol ((*E*)-8m): ^{1}H NMR δ 0.87 (3 H, t, J = 7.4 Hz), 0.90 (3 H, t, J = 7.4 Hz), 1.01 (3 H, d, J = 6.6 Hz), 1.02–2.20 (13 H, m), 2..0 (1 H, br d, J = 12.6 Hz), 5.00 (1 H, s); IR (liquid film) (mixture of E and Z isomers) 3470 (br), 1670 (s), 1145 (s), 960 cm^{-1} (s); mass spectrum, m/z (relative intensity) 196 (M$^+$, <1), 178 (2), 167 (100), 153 (13), 121 (3), 109 (8); exact mass calcd for $C_{13}H_{24}O$ 196.1828 (found 196.1822).

(*Z*)-3-[(2-Methylcyclohexylidene)methyl]-3-pentanol ((*Z*)-8m): ^{1}H NMR δ 0.87 (3 H, t, J = 7.5 Hz), 0.89 (3 H, t, J = 7.5 Hz), 1.07 (3 H, d, J = 7.2 Hz), 1.08–1.92 (12 H, m), 2.26 (1 H, ddt, J = 1.8, 4.5, and 13.7 Hz), 3.43 (1 H, m), 5.00 (1 H, d, J = 1.8 Hz); mass spectrum, m/z (relative intensity) 196 (M$^+$, <1), 178 (3), 167 (100), 149 (8), 121 (3), 109 (8); exact mass calcd for $C_{13}H_{24}O$ 196.1828 (found 196.1823).

1-(2,4,6-Trimethylphenyl)pentanol (9a): ^{1}H NMR δ 0.88 (3 H, br t, J = 7.6 Hz), 1.02–2.04 (7 H, m), 2.23 (3 H, s), 2.38 (6 H, s), 5.12 (1 H, dd, J = 5.6 and 8.6 Hz), 6.80 (2 H, s); IR (liquid film) 3400 (br), 1620 (s), 1050 (s), 1010 (m), 850 cm^{-1} (s); mass spectrum, m/z (relative intensity) 206 (M$^+$, 8), 188 (6), 150 (100), 121 (88).

(1*R,2*S**,5*R**)-2-Isopropyl-5-methyl-1-(2-methyl-1-propenyl)cyclohexanol (12)**: ^{1}H NMR δ 0.82 (3 H, d, J = 6.8 Hz), 0.84 (3 H, d, J = 6.5 Hz), 0.95 (3 H, d, J = 6.9 Hz), 1.0–2.0 (16 H, m, including br s (3 H) at 1.71 and br s (3 H) at 1.89), 5.41 (1 H, br s); ^{13}C NMR 19.0, 19.3, 22.5, 24.3, 24.5, 26.4, 27.8, 30.4, 35.1, 51.2, 54.7, 76.2, 126.2, 134.2; IR (liquid film) 3460 (br), 1670 (m), 1030 cm^{-1} (m); mass spectrum, m/z (relative intensity) 210 (M$^+$, 9), 195 (8), 192 (59), 177 (64), 125 (100); exact mass calcd for $C_{14}H_{26}O$ 210.1985 (found 210.1987).

(1*S,2*S**,5*R**)-2-Isopropyl-5-methyl-1-(2-methyl-1-propenyl)cyclohexanol (13)**: ^{1}H NMR δ 0.83 (3 H, d, J = 6.7 Hz), 0.86 (3 H, d, J = 6.9 Hz), 0.87 (3 H, d, J = 7.2 Hz), 1.1 (2 H, m), 1.23 (1 H, s), 1.45 (3 H, m), 1.70 (3 H, br s), 1.75 (3 H, m), 1.89 (3 H, br s), 2.03 (1 H, d sept, J = 1.0 and ~7 Hz), 5.41 (1 H, br s); ^{13}C NMR 18.7, 18.9, 21.0, 22.3, 24.1, 27.0, 27.7, 27.9, 35.0, 48.6, 50.5, 77.1, 132.2, 132.7; IR (liquid film) 3480 (br), 1660 cm^{-1} (m); mass spectrum, m/z (relative intensity) 210 (M$^+$, 13), 195 (11), 192 (12), 177 (11), 125 (100); exact mass calcd for $C_{14}H_{26}O$ 210.1985 (found 210.1987). Anal. Calcd for $C_{14}H_{26}O$: C, 79.93; H, 12.46. Found: C, 80.22; H, 12.63.

(1*S,2*S**,5*R**)-1-Butyl-2-isopropyl-5-methylcyclohexanol (14)**: ^{1}H NMR δ 0.75 – 1.80 (27 H, m, including d (3 H, J = ~7 Hz) at 0.84, d (3H, J = 7.0 Hz) at 0.86, and d (3 H, J = 6.8 Hz) at 0.87), 2.06 (1 H, d sept, J = 1.8 and ~7 Hz); IR (liquid film) 3520 (s), 960 cm^{-1} (m); mass spectrum, m/z (relative intensity) 212 (M$^+$, <1), 155 (26), 127 (100), 81 (50).

Reaction of Menthyl Oxide (11; M = Li) with Isopropylidenemethylene Carbenoid (1) at −85 °C. To a solution of 11 (M = Li) (4.0 mmol) and chloride **5a** (0.20 mL, 2.0 mmol) in THF (8 mL) was added n-BuLi (2.2 mmol) at −85 °C. After being stirred for 0.5 h at the same temperature, the mixture was allowed to warm to the room temperature over a period of 14 h. The usual workup followed by flash chromatography (5%) gave 124.8 mg (total yield 30%) of a 47:12:41 mixture of **12**, **13**, and **14**.

By a similar procedure, 1.74 mmol of lithium menthyl-*1-d* oxide (d content >95%) and 0.87 mmol (86 μL) of **5a** were treated with n-BuLi (0.96 mmol) in THF (3.5 mL) to give 25.6 mg of a 47:9.6:44 mixture of **12-*d***, **13-*d***, and **14**. The mixture was separated into a mixture of **13-*d*** and **14**, and pure **12-*d***. The deuterium content of **12** and **13** at their vinylic positions were measured by the ^{1}H NMR spectra of these samples.

Crossover Reaction of Benzyl-α,α-d_2 Oxide (4a-d_2; M = K) and 4-Chlorobenzyl Oxide (4b; M = K) with Isopropylidenemethylene Carbenoid at 0 °C. A THF (5 mL) solution of **4a**-d_2 (M = K) (d content >95%) (1.00 mmol), **4b** (M = K) (1.00 mmol), and **5a** (4.00 mmol) was treated with n-BuLi (4.00 mmol) at 0 °C for 15 min. After the usual workup followed by flash chromatography (10–20%), 130 mg of a mixture of **8a**-d_2 (31% yield based on the starting alcohol) and **8d** (42% yield based on the starting alcohol) was obtained. These product alcohols were transformed to the corresponding methyl ethers as follows. To a THF suspension of KH (58.2 mg, 0.508 mmol) in THF (1.0 mL) was added a THF (0.3 mL) solution of 40.0 mg of the above mixture of **8a**-d_2 and **8d** at 0 °C. After stirring for 30 min, 55 μL (0.88 mmol) of iodomethane was added to the mixture, and the mixture was stirred further for 20 min. The usual workup followed by flash chromatography (5%) gave 31.5 mg of a mixture of two methyl ethers which were separated by preparative GLC and analyzed by ^{1}H NMR measurement. 1-Methoxy-3-methyl-1-phenyl-2-butene-*1,2-d*$_2$: ^{1}H NMR δ 1.73 (3 H, s), 1.78 (3 H, s), 3.28 (3 H, s), 7.32 (5 H, m). 1-Methoxy-3-methyl-1-phenyl-2-butene: ^{1}H NMR (60 MHz) δ 1.76 (6 H, d, J = 1.5 Hz), 3.28 (3 H, s), 4.76 (1 H, d, J = 8.8 Hz), 5.29 (1 H, d sept, J = 8.8 and 1.5 Hz), 7.3 (5 H, m).

1-(4-Chlorophenyl)-1-methoxy-3-methyl-2-butene: ^{1}H NMR δ 1.72 (3 H, d, J = 1.5 Hz), 1.75 (3 H, d, J = 1.5 Hz), 3.27 (3 H, s), 4.85 (1 H, d, J = 8.8 Hz), 5.24 (1 H, d sept, J = 8.8 and 1.5 Hz), 7.27 (4 H, m).

Reaction of Potassium Menthyl Oxide (10; M = K) with Isopropylidenemethylene Generated from 2-Methylpropenyl Trifluoromethanesulfonate. To a solution of alkoxide 11 (M = K) (2.5 mmol) and t-BuOK (135 mg, 1.20 mmol) in THF (5 mL) was added a THF (1 mL) solution of 204 mg (1 mmol) of 2-methylpropenyl trifluoromethanesulfonate at 0 °C, and the mixture was stirred at the same temperature for 1 h. The usual workup followed by separation by flash chromatography (2–5%) gave, in order of elution, 56.3 mg (27%) of menthyl 2-methylpropenyl ether (**18**), 32.4 mg (11%) and 4-(menthyloxy)butyl 2-methylpropenyl ether (**17**), 6.7 mg (3%) of **12**, and 287.1 mg of menthol. Capillary GC (PEG) analysis of the reaction mixture showed the presence of menthone (2%).

17: ^{1}H NMR δ 0.74 (3 H, d, J = 6.9 Hz), 0.84 (3 H, d, J = 7.2 Hz), 0.89 (3 H, d, J = 6.6 Hz), 0.9–1.8 (17 H, m, including d (3 H, J = 1.4 Hz) at 1.51 and d (3 H, J = 1.4 Hz) at 1.58), 2.06 (1 H, br d, J = ~13 Hz), 2.19 (1 H, d sept, J = 2.6 and ~7 Hz), 2.97 (1 H, dt, J = 4.2 and 10.6 Hz), 3.26 (1 H, m), 3.64 (3 H, m), 5.76 (1 H, sept, J = 1.4 Hz); IR (liquid film) 1705 (s), 1175 (s), 1120 cm^{-1} (s); mass spectrum, m/z (relative intensity) 282 (M$^+$, 1), 212 (4), 211 (29), 139 (96), 57 (100); exact mass calcd for $C_{18}H_{34}O_2$ 282.2559 (found 282.2577).

18: ^{1}H NMR (60 MHz, CCl_4) δ 0.6–2.6 (18 H, m), 1.72 (6 H, br s), 2.99 (1 H, dt, J = 4 and 10 Hz), 3.63 (1 H, br d, J = ~12 Hz), 3.99 (1 H, br d, J = ~12 Hz, 4.82 (2 H, m); IR (liquid film) 1660 (s), 1460 (s), 1380 (s), 1120 (s), 900 cm^{-1} (s).

General Procedure for the Reactions of Alkoxides with (2,3-Benzo-2-cyclohexylidene)methylene Carbenoid (3) at Low Temperatures. These reactions were performed by using the apparatus shown in Figure 2. To a solution of **7b** (1.00 mmol) in THF (1.5 mL) prepared in the right-side flask was added slowly

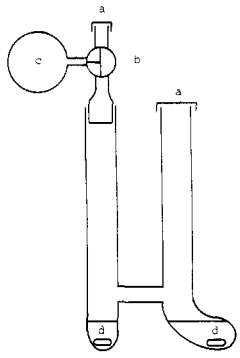

Figure 2. (a) Septum rubber; (b) three-way stopcock; (c) nitrogen balloon; (d) magnetic stirring bar.

n-BuLi (1.00 mmol) at −95 °C (toluene–liquid nitrogen bath), and the resulting dark blue solution was stirred for 1 h at the same temperature. A THF (1.0 mL) solution of alkoxide 4 (M = Li) (2.00 mmol) prepared in the left-side flask was transfered to the right-side flask by tilting the apparatus in the cooling bath, the flask was quickly immersed in the other bath which was cooled at −85 °C, and the mixture was allowed to warm from −85 to −40 °C over a period of 1–2 h. after the usual workup followed by flash chromatography, a mixture of the insertion products (*E*)-8 and (*Z*)-8 was obtained. The ratio of (*E*)- and (*Z*)-8 was determined by ^{1}H NMR integration. The separation of the isomer was performed by using medium-pressure column chromatography. Spectral data of new compounds are as follows.

(*E*)-3-[(2,3-Benzo-2-cyclohexylidene)methyl]-3-pentanol ((*E*)-8n): ^{1}H NMR δ 0.98 (6 H, t, *J* = 7.4 Hz), 1.57 (1 H, br s), 1.73 (2 H, q, *J* = 7.4 Hz), 1.74 (2 H, q, *J* = 7.6 Hz), 1.87 (2 H, quint, *J* = 6.2 Hz), 2.77–2.92 (4 H, m), 5.91 (1 H, br s), 7.05–7.22 (3 H, m), 7.54 (1 H, m); IR (liquid film) 3450 (br), 1120 (s), 1025 (s), 985 (s), 950 (s), 915 (s), 755 (s), 735 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 230 (M$^+$, 2), 201 (100), 183 (10); exact mass calcd for $C_{16}H_{22}O$ 230.1672 (found 230.1661).

(*Z*)-3-[(2,3-Benzo-2-cyclohexylidene)methyl]-3-pentanol ((*Z*)-8n): ^{1}H NMR δ 0.89 (6 H, t, *J* = 7.4 Hz), 1.25 (1 H, br s), 1.62 (4 H, q, *J* = 7.6 Hz), 1.86 (2 H, quint, *J* = 6.9 Hze, 2.36 (2 H, br t, *J* = 7.0 Hz), 2.72 (2 H, t, *J* = 6.6 Hz), 5.34 (1 H, br s), 7.05–7.24 (3 H, m), 7.59 (1 H, m); IR (liquid film) 3600 (br), 3470 (br), 1605 (s), 1040 (s), 990 (s), 950 (s), 910 (s), 765 (s), 740 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 230 (M$^+$, 1), 201 (100), 183 (17); exact mass calcd for $C_{16}H_{22}O$ 230.1672 (found 230.1678).

(*E*)-(1*R,2*S**,3*R**)-1-[(2,3-Benzo-2-cyclohexylidene)-methyl]-2-isopropyl-5-methylcyclohexanol ((*E*)-20)**: R_f 0.42 (silica, 20% ether in petroleum ether), R_f 0.45 (silica, 30% petroleum ether in benzene); ^{1}H NMR δ 0.86 (3 H, d, *J* = 6.6 Hz), 0.93 (3 H, d, *J* = 7.0 Hz), 1.01 (3 H, d, *J* = 7.0 Hz), 1.07–1.98 (10 H, m), 2.00–2.19 (2 H, m), 2.81 (3 H, m, including t (2 H, *J* = 7.2 Hz) at 2.82), 3.06 (1 H, dddd, *J* = 1.3, 4.4, 7.0 and 14.6 Hz), 6.20 (1 H, br s), 7.03–7.21 (3 H, m), 7.48 (1 H, m); ^{13}C NMR δ 19.4, 22.5, 23.6, 24.4, 24.6, 26.7, 27.2, 30.1, 30.5, 35.0, 51.1, 55.2, 76.8, 124.2, 125.9, 126.9, 129.1, 137.4, 137.57, 137.64; IR (liquid film) 3450 (br), 1630 (s), 1160 (s), 1120 (s), 1040 (s), 1010 (s), 910 (s), 850 (s), 750 (s), 730 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 298 (M$^+$, 18), 280 (3), 213 (45), 185 (100), 171 (29), 130 (35); exact mass calcd for $C_{21}H_{30}O$ 298.2298 (found 298.2295).

(*Z*)-(1*R,2*S**,3*R**)-1-[(2,3-Benzo-2-cyclohexylidene)-methyl]-2-isopropyl-5-methylcyclohexanol ((*Z*)-20)**: R_f 0.64 (silica, 20% ether in petroleum ether), R_f 0.54 (silica, 30% petroleum ether in benzene); ^{1}H NMR δ 0.85 (3 H, d, *J* = 7.2 Hz), 0.87 (6 H, d, *J* = 6.8 Hz), 1.13–2.13 (12 H, m), 2.36 (2 H, m), 2.71 (2 H, t, *J* = 6.8 Hz), 5.77 (1 H, br s), 7.05–7.21 (3 H, m), 7.55 (1 H, m); ^{13}C NMR δ 18.8, 22.6, 23.8, 24.2, 26.1, 29.0, 30.3, 35.1, 35.8, 52.5, 54.3, 125.0, 127.5, 127.7, 128.0, 128.7, 135.1, 137.1, 139.6; IR (liquid film) 3580 (s), 3470 (br), 1050 (s), 1010 (s), 985 (s), 950 (s), 930 (s), 885 (s), 855 (s), 765 (s), 755 (s), 725 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 298 (M$^+$, 7), 237 (5), 213 (53), 185 (100), 171 (40); exact mass calcd for $C_{21}H_{30}O$ 298.2298 (found 298.2298).

(*E*)-(1*S,2*S**,3*R**)-1-[(2,3-Benzo-2-cyclohexylidene)-methyl]-2-isopropyl-5-methylcyclohexanol ((*E*)-21)**: R_f 0.61 (silica, 20% ether in petroleum ether), R_f 0.63 (silica, 30% petroleum ether in benzene); ^{1}H NMR δ 0.89 (3 H, d, *J* = 7.0 Hz), 0.93 (3 H, d, *J* = 7.0 Hz), 0.94 (3 H, d, *J* = 7.0 Hz), 0.98–1.93 (11 H, m), 2.10 (1 H, d sept, *J* = 1.6 and 6.8 Hz), 2.81 (2 H, t, *J* = 6.6 Hz), 2.88 (2 H, m), 5.90 (1 H, br s), 7.03–7.21 (3 H, m), 7.49 (1 H, m); ^{13}C NMR δ 1.91, 21.2, 22.3, 23.7, 24.3, 26.7, 27.6, 27.8, 30.1, 35.1, 48.2, 51.0, 78.1, 124.4, 125.9, 126.8, 129.0, 132.1, 136.0, 137.50, 137.53; IR (liquid film) 3590 (br), 3490 (br), 1625 (m), 1170 (s), 1110 (s), 1030 (s), 1010 (s), 975 (s), 940 (s), 840 (s), 805 (s), 745 (s), 715 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 298 (M$^+$, 16), 213 (49), 185 (100), 171 (29), 130 (25); exact mass calcd for $C_{21}H_{30}O$ 298.2298 (found 298.2297). Anal. Calcd for $C_{21}H_{30}O$: C, 84.51; H, 10.13. Found: C, 84.47; H, 10.22.

(*Z*)-(1*S,2*S**,3*R**)-1-[(2,3-Benzo-2-cyclohexylidene)-methyl]-2-isopropyl-5-methylcyclohexanol ((*Z*)-21)**: R_f 0.77 (silica, 20% ether in petroleum ether); ^{1}H NMR δ 0.79 (3 H, d, *J* = 7.0 Hz), 0.86 (3 H, d, *J* = 5.4 Hz), 0.86 (3 H, d, *J* = 7.0 Hz), 1.08–1.95 (11 H, m), 2.05 (1 H, d sept, *J* = 1.9 and 6.7 Hz), 2.34 (2 H, m), 2.69 (2 H, t, *J* = 6.9 Hz), 5.36 (1 H, br s), 7.03–7.25 (3 H, m), 7.50 (1 H, m); ^{13}C NMR δ 18.7, 20.9, 22.3, 22.8, 24.0, 27.60, 27.64, 29.0, 35.2, 35.3, 49.9, 51.2, 75.8, 125.0, 127.4, 127.6, 128.3, 134.0, 134.8, 137.0, 139.7; IR (liquid film) 3590 (s), 1600 (s), 1045 (s), 980 (s), 945 (s), 910 (s), 810 (s), 755 (s), 735 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 298 (M$^+$, 6), 213 (49), 185 (100), 171 (40); exact mass calcd for $C_{21}H_{30}O$ 298.2298 (found 298.2298).

Crossover Reaction of Cyclohexyl-*1*-*d* Oxide (4f-*d*; M = Li) and 3-Pentyl Oxide (4g; M = Li) with (2,3-Benzo-2-cyclohexylidene)methylene Carbenoid (3). A THF (2.5 mL) solution of **4f**-*d* (M = Li) (*d* content >99%) (1.02 mmol), **4g** (M = Li) (1.01 mmol), and chloride **7b** (216 mg, 1.01 mmol) was treated with *n*-BuLi (1.01 mmol) at 0 °C following the general procedure described before. Separation of the crude mixture by flash chromatography (3–12% ether in petroleum ether) gave, in order of elution, 15.6 mg of (*Z*)-**8n**, 6.4 mg of (*Z*)-**8k**-*d*, and 86.8 mg of a mixture of (*E*)-**8n** and (*E*)-**8k**-*d*. Capillary GLC analysis of the reaction mixture showed the formation of butyl adducts **9b** and **9c** in 1.1% and 8.6% yield, respectively. Deuterium content of each product was determined by integration in the ^{1}H NMR spectra of these samples.

Following the general reaction procedure at low temperatures described before, a solution of **4f**-*d* (M = Li) (1.01 mmol) and **4g** (M = Li) (1.02 mmol) in THF (1.0 mL) was mixed with a solution of ((2,3-benzo-2-cyclohexylidene)chloromethyl)lithium prepared by the reaction of dichloride **7b** (211 mg, 0.991 mmol) with *n*-BuLi (0.99 mmol) in THF (1.5 mL) at −95 °C. The crude mixture was subjected to flash chromatography (3–12% ether in petroleum ether) to give 124.5 mg of a mixture of (*E* and *Z*)-**8k**-*d* (23%) and (*E* and *Z*)-**8n** (31%) ((*E*)-**8n**:(*Z*)-**8n** = 7.56:1). The ^{1}H NMR spectrum of the mixture showed <3% deuterium incorporation at the vinylic position of (*E* and *Z*)-**8k**-*d*.

Crossover Reaction of Cyclohexyl Oxide (4f; M = Li) and 3-Pentyl-*3*-*d* Oxide (4g-*d*; M = Li) with (2,3-Benzo-2-cyclohexylidene)methylene Carbenoid. By the similar procedure, a solution of **4f** (M = Li) (1.04 mmol) and **4g**-*d* (M = Li) (*d* content >99%) (1.07 mmol) in THF (1.0 mL) was treated with ((2,3-benzo-2-cyclohexylidene)chloromethyl)lithium prepared from **7b** (213 mg, 1.00 mmol) at −95 °C. Separation by flash chromatography (3–12% ether in petroleum ether) gave, in order of elution, 11.1 mg of (*Z*)-**8n**-*d*, 13.0 mg of (*Z*)-**8k**, and 97.7 mg of a mixture of (*E*)-**8n**-*d* and (*E*)-**8k**.

Preparation of ((2,3-Benzo-2-cyclohexylidene)chloromethyl)lithium. To a solution of dichloride **7b** (211 mg, 0.992 mmol) in THF (2.5 mL) was added *n*-BuLi (0.992 mmol) at −95 °C, and the mixture was stirred for 1 h. The reaction was quenched by the addition of cooled 20% acetic acid in THF. The yields of (*E*)-**7a** (89%) and (*Z*)-**7a** (1.6%) were determined by the ^{1}H NMR spectrum of the crude mixture by using durene as the internal standard.

Reaction of ((2,3-Benzo-2-cyclohexylidene)chloromethyl)lithium with Benzaldehyde. To a solution of **7a** (*E*:*Z* = 84:16) (192 mg, 1.08 mmol) in THF (2.5 mL) was added *n*-BuLi (1.08 mmol) at −95 °C, and the mixture was stirred for 6.5 h at the same temperature. To this was added a THF (1.0 mL) solution of benzaldehyde (0.11 mL, 1.1 mmol) at −95 °C, and the mixture was stirred further for 10 min. After the usual workup followed by flash chromatography (7%), 270.8 mg (88%) of (*E*)-2-(2,3-benzo-2-cyclohexylidene)-2-chloro-1-phenylethanol (**22**) was ob-

tained. The ^{1}H NMR spectrum of the reaction mixture showed the recovery of (*E* and *Z*)-**7a** (6.1%, *E*:*Z* = 2.1:1). **22**: ^{1}H NMR δ 1.78–1.98 (3 H, m), 2.69 (2 H, t, *J* = 6.2 Hz), 2.80 (2 H, t, *J* = 6.9 Hz), 6.15 (1 H, d, *J* = 8.0 Hz), 7.11–7.52 (9 H, m); IR (liquid film) 3545 (br), 3400 (br), 1605 (s), 1115 (s), 1095 (s), 1075 (s), 1025 (s), 995 (s), 925 (s), 840 (s), 760 (s), 750 (s), 700 (s), 660 cm^{-1} (s); mass spectrum, *m*/*z* (relative intensity) 286 (M^+, $C_{18}H_{17}O^{37}Cl$, 3), 284 (M^+, $C_{18}H_{17}O^{35}Cl$, 9), 294 (14), 231 (10), 118 (31), 107 (100), 91 (25); exact mass calcd for $C_{18}H_{17}O^{37}Cl$ 286.0939 and $C_{18}H_{17}O^{35}Cl$ 284.0969 (found 286.0938 and 284.0970).

Reaction of Menthone with (2-Methylpropenyl)lithium. To a THF (5 mL) solution of menthone (168.6 mg, 1.09 mmol) was added 1.10 mmol of 2-propenyllithium (0.196 M in THF–pentane) at 0 °C, and the mixture was stirred for 5 min. After the usual workup the crude mixture was analyzed by capillary GLC (PEG-20M). Reaction of menthone with *n*-BuLi was performed by a similar procedure.

Reaction of Menthone with ((2,3-Benzo-2-cyclohexylidene)methyl)magnesium Chloride. The Grignard reagent was prepared by refluxing a THF (7.5 mL) mixture of magnesium turnigs (144 mg, 6.00 mmol) and **7a** (*E*:*Z* = 84:16) (538 mg, 3.01 mmol) in the presence of several milligrams of iodine. To this was added 924 mg (5.92 mmol) of menthone, and the mixture was heated under reflux for 0.5 h. The usual workup followed by flash chromatography (1–10% ether in petroleum ether) gave 178.2 mg (20%) of (*E*)-**21** and 11.7 mg (1.3%) of (*Z*)-**21**.

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Registry No. **4a**·K, 22379-62-0; **4a**·Li, 15082-42-5; **4a**-d_2, 114507-60-7; **4b**·K, 73447-13-9; **4c**·K, 95465-43-3; **4d**·K, 2245-69-4; **4e**·K, 114507-39-0; **4f**·K, 54637-77-3; **4f**·Li, 4111-51-7; **4f**-*1*-*d*, 114507-68-5; **4g**·K, 78278-74-7; **4g**·Li, 15675-21-5; **4g**-*3*-*d*, 114507-71-0; **5a**, 513-37-1; **5b**, 3017-69-4; (*E*)-**6a**, 68089-82-7; (*Z*)-**6a**, 68089-83-8; **66**, 57124-78-4; (*E*)-**7a**, 114507-40-3; (*Z*)-**7a**, 114507-41-4; **7b**, 91092-18-1; **8a**, 95465-44-4; **8a**-d_2, 114507-61-8; (*E*)-**8c**, 114507-45-8; (*Z*)-**8c**, 114507-46-9; **8d**, 95465-56-8; **8e**, 95465-46-6; **8f**, 62217-47-4; **8h**, 114507-49-2; **8i**, 6244-46-8; (*E*)-**8j**, 114507-50-5; (*Z*)-**8j**, 114507-51-6; (*E*)-**8k**, 114507-52-7; (*E*)-**8k**-*d*, 114507-70-9; (*Z*)-**8k**, 114507-53-8; (*Z*)-**8k**-*d*, 114507-69-6; (*E*)-**8n**, 114507-56-1; (*E*)-**8n**-*d*, 114507-73-2; (*Z*)-**8n**, 114507-57-2; (*Z*)-**8n**-*d*, 114507-72-1; (*E*)-**8m**, 114507-54-9; (*Z*)-**8m**, 114507-55-0; **9a**, 95465-55-7; **9b**, 5445-30-7; **9c**, 19780-41-7; (*E*)-**10b**, 114507-43-6; (*Z*)-**10b**, 114507-44-7; (*E*)-**10g**, 114507-47-0; (*Z*)-**10g**, 114507-48-1; **11**·Li, 95465-51-3; **11**·K, 95465-47-7; **11**-*d*·K, 114507-58-3; **12**, 95465-48-8; **12**-*d*, 95483-62-8; **13**, 95465-49-9; **14**, 95465-50-2; **15**, 114507-59-4; **16**, 53282-30-7; **17**, 95465-54-6; **18**, 114507-63-0; (*E*)-**20**, 114507-64-1; (*Z*)-**20**, 114507-65-2; **19**, 114507-42-5; (*E*)-**21**, 114507-66-3; (*Z*)-**21**, 114507-67-4; **22**, 114507-74-3; 1-methoxy-3-methyl-1-phenyl-2-butene-*1*,*2*-d_2, 114507-62-9; 1-methoxy-3-methyl-1-phenyl-2-butene, 83605-31-6; menthone, 89-80-5; ((2,3-benzo-2-cyclohexylidene)methyl)magnesium chloride, 114507-75-4; 1-(4-chlorophenyl)-1-methoxy-3-methyl-2-butene, 114507-76-5.

Formation of 1-Phenyl-2,3-dioxabicyclo[2.2.1]heptane in the Reaction of 1,3-Dibromo-4-phenylcyclopentane with Hydrogen Peroxide in the Presence of Silver Trifluoroacetate†

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Reaction of 1,3-dibromo-4-phenylcyclopentane (**23**), prepared from 4-hydroxycyclopent-2-en-1-one (**10**) in a stereocontrolled manner, or its stereoisomer **24** with anhydrous hydrogen peroxide in the presence of silver trifluoroacetate in ether gave 1-phenyl-2,3-dioxabicyclo[2.2.1]heptane (**25**) mainly as a rearranged product. The expected 5-phenyl-2,3-dioxabicyclo[2.2.1]heptane (**8**) and phenylcyclopentenyl hydroperoxides **26** and **27** were also formed in this reaction. An authentic sample of endoperoxide **8** was prepared by using peroxide transfer reaction between bis(tri-*n*-butyltin) peroxide and bistriflate of *cis*-diol **35**. The stereochemistry of the endoperoxide **8** and related compounds in this series was confirmed by correlation with the data from X-ray crystallographic analysis of the diacetate of diol **21** obtained from endoperoxide **8** by stannous chloride reduction.

Since the time prostaglandin endoperoxides PGG_2 (**1**) and PGH_2 (**2**) were isolated and characterized by Hamberg and Samuelsson[1] in 1973, the chemistry of endoperoxides has been studied extensively.[2,3] Several methods have been developed for the synthesis of endoperoxides. The simplified endoperoxide 2,3-dioxabicyclo[2.2.1]heptane (**3**) was synthesized as a model compound for PG endoperoxides **1** and **2**. Salomon and Salomon[4] reported the synthesis of **3** by peroxide transfer reaction between the bistriflate of cyclopentane-1,3-diol and bis(tri-*n*-butyltin) peroxide. Porter and Gilmore[5] reported synthesis of **3** by intramolecular cyclization of 3-bromocyclopentane 1-hydroperoxide, or by the double displacement reaction of 1,3-dibromocyclopentane with hydrogen peroxide in the presence of silver acetate. Adam and Eggelte[6] reported a simple synthesis of **3** from cyclopentadiene using singlet oxygen followed by diimide reduction. Recently, **3** was synthesized from bicyclo[2.1.0]pentane via *tert*-butyl peroxymercuriation by Bloodworth and Hargreaves.[7] The trapping of triplet cyclopentane-1,3-diyl with oxygen to

† All compounds described in this paper are racemic, and one series of enantiomers is depicted for convenience.

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§ Laboratory of Physical Chemistry.

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